The Absorption of X-Rays.

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(Communicated by Prof. A. W. Porter, F.R.S. Received March 13, 1918.)

Introduction.—Previous to the discovery of the behaviour of X-rays with regard to crystals, the most homogeneous radiation obtainable was that of the characteristic radiation of an element which is excited when that element is exposed to X-radiation of suitable hardness. These characteristic radiations are now found, however, by the new method of analysis, to be constituted of a number of radiations of different wave-lengths. Moseley,* shortly after the discovery of the reflection of X-rays, showed that the characteristic radiations of most of the metals he examined consisted of two prominent wave-lengths; Bragg† later found that, in the case of rhodium, palladium and silver, each of these lines could be further resolved into two components. Hence the spectra of the characteristic radiation of the K series of these elements consist of at least four different wave-lengths. The analysis of a beam of X-rays into its constituent radiations by reflection at a crystal face provides a means, therefore, of obtaining radiation of a definite wave-length and of such intensity as to enable its absorption coefficient in different materials to be accurately measured.

Bragg and Pierce‡ have already measured the absorption coefficients of the two most prominent lines in the spectra of the elements Rh, Pd and Ag, in a number of metals. To make the absorption coefficient more directly comparable with other atomic characteristics, they gave their results in the form of atomic absorption coefficients: the atomic absorption coefficient expresses the proportion of the energy of an X-ray pencil which is absorbed in crossing a surface on which lies one atom to every square centimetre. The ordinary mass absorption coefficient can be calculated from this quantity by dividing it by the mass of the absorbing atom. The experimental results showed that the ratio of two absorption coefficients is independent of the wave-length of the radiation over considerable ranges, a result previously deduced by Barkla from his experiments; also, that the atomic absorption coefficient is proportional to the fourth power of the atomic number of the absorber.

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* Moseley, 'Phil. Mag.,' vol. 26, p. 1024 (1913).

† W. H. Bragg, 'Phil. Mag.,' vol. 29, p. 407 (1915).

‡ Bragg and Pierce, 'Phil. Mag.,' vol. 28, p. 626 (1914).

Combining this last result with the existing relation connecting the absorption coefficient with the wave-length of the radiation, namely—

$$\text{Mass absorption coefficient} \propto \lambda^{5/2},$$

Bragg and Pierce arrived at the following very general law

$$\text{Atomic absorption coefficient} = \mathrm{CN}^4\lambda^{5/2},$$

where N is the atomic number of the absorber, and λ the wave-length of the radiation. The quantity C is constant over considerable ranges but changes abruptly when we get into the region of selective absorption.

Some doubt has been cast on the validity of the above relation connecting atomic number and atomic absorption coefficient by the results of Auren,* who has recently made an extensive investigation of the absorption of a great number of solutions. On the assumption that the molecular absorption coefficient can be obtained by adding together the atomic absorption coefficients of the atoms composing the molecule, it has been possible, from the observed values of the molecular absorption coefficients of the different substances used, to calculate the relative atomic absorption coefficients of the elements from hydrogen upwards. In the experiment, rays direct from a bulb with tungsten anticathode were employed which had been passed through an aluminium screen 1·25 mm. thick to filter away rays of the longer wave-lengths in the beam. A measurement of the wave-length of the radiation transmitted gave a mean value of $0{\cdot}35 \times 10^{-8}$ cm.

To determine the absorption coefficient of a certain molecule, solutions of different concentrations containing that molecule were taken, from which a fairly accurate mean value of the molecular absorption coefficient could be obtained. From these observed results the relative values of the atomic absorption coefficient of the elements were calculated by assuming the additive law just mentioned. The final results led to the conclusion that the atomic absorption coefficient is not proportional to the fourth power of the atomic number, but that the elements divide up into groups, for each of which the atomic absorption coefficient is directly proportional to the atomic number.

The object of this paper is to endeavour to account for these two discordant results. A general law is arrived at which differs slightly from that stated by Bragg and Pierce, by the aid of which the molecular absorption coefficients of all the substances used by Auren have been calculated for the wave-length employed by him and the values thus obtained are all found to agree, within the limits of experimental error, with those actually observed in Auren's experiment.

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* Auren, 'Phil. Mag.,' vol. 33, p. 471 (1917).

Experimental.—In the experimental part of the present investigation, particular attention is paid to the absorption of the α-line of palladium in different substances. This line was chosen because its mean wave-length is known very accurately, and its intensity, when reflected from the (111) face of a crystal of carborundum, is so great as to enable measurements of its absorption in different substances to be made with accuracy. Also, the intensity of the superposed second and third order spectra of the shortest wave-lengths in the spectrum of the radiation emitted by the bulb was so small compared with the intensity of the α-line itself that it had no appreciable effect upon the purity of the α-radiation.*

The carborundum crystal was placed on the revolving table of the X-ray spectrometer, and fixed in the position in which it reflected the α-line of palladium into the ionisation chamber. By the arrangement of slits adopted in the experiment, the reflected beam was confined to a very narrow pencil, so that the width of the chamber slit could be made very narrow without appreciably cutting down the intensity of the beam that entered the ionisation chamber. Its width was fixed at 0·4 mm. The employment of a slit so narrow as this adds to the accuracy of the determination of the absorption coefficient. In the measurement of absorption coefficients, it is important to prevent secondary radiation, either scattered or fluorescent produced by the primary radiation, from entering the ionisation chamber. When the rays traverse the absorbing screen, it is required to find the intensity of the radiation which proceeds as primary radiation after passing through the screen. By using a narrow slit, the experimental conditions necessary for this are approximately obtained. These conditions may be further improved by removing the screen a little distance away from the chamber slit, in which case only the secondary radiation contained in the small solid angle subtended at the slit by the illuminated portion of the absorbing screen enters the chamber, and in this particular case this would be negligible. Experiment showed that there was no difference in the value of the absorption coefficient obtained when the absorbing screen was moved from a position about 2 cm. in front of the chamber slit to a position near the crystal. In the present investigation, the absorbing screens were all placed about 2 cm. in front of the chamber slit when their absorption coefficients were being measured.

The substances whose absorption coefficients are measured range from zinc down to light substances containing carbon and oxygen, such as filter paper and water; it is the values of the absorption coefficients of the lightest substances that suggest a possible explanation of the disagreement for which we are seeking to account.

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* See Owen, 'Roy. Soc. Proc.,' A, vol. 94, p. 347 (1918).

It will be assumed that water and filter paper behave like elements whose atomic numbers are 8 and 7 respectively. In water oxygen absorbs most of the radiation, the absorption due to hydrogen being almost negligible in comparison with it; in filter paper, whose constitution may be represented by the formula $n(C_6H_{10}O_5)$, the mass of the carbon atoms is not much smaller than that of the oxygen atoms, so that the substance may be taken to behave towards X-rays as an element whose atomic number is the mean of those of carbon and oxygen, *e.g.*, of atomic number 7. These approximate assumptions are made here to enable us to plot the absorption coefficients of these substances on the same graph as those for the elements employed, in order to get a rough idea of the shape of the absorption curve in this region. Later, the actual value of the molecular absorption coefficient of each substance will be calculated, in which case account will be taken of the absorption of the hydrogen atom whose effect is being ignored in making the above assumptions.

The values of the absorption coefficients are obtained from the usual relation $I = I_0 e^{-\mu x}$, where I_0 is the intensity of the primary radiation before, and I its intensity after traversing a screen of thickness x cm.

The final mean values experimentally obtained are tabulated in Table I; they are the mean of a large number of observations. The results previously obtained by Bragg and Pierce with the α-line of palladium are also included in the Table for comparison, and it will be observed that the values obtained now agree fairly closely with their values for the elements used in common. In view of this corroboration of Bragg and Pierce's results, it was not considered necessary to extend the investigation to other wave-lengths, as the information obtained with the α-palladium radiation sufficed for the immediate purpose in view.

Table I.

Absorber.	Atomic number.	μ/ρ.			
		Owen.	Bragg and Pierce.	Hull and Rice.	Mean values.
Zn	30	34·7	34·0	—	34·3
Cu	29	29·5	30·9	30·28	30·2
Ni	28	26·0	28·9	—	27·4
Fe	26	—	23·1	—	23·1
Al	13	3·11	3·16	3·12	3·13
Mg	12	2·43	—	—	2·43
Water	[8]	0·844	—	—	0·844
Filter paper	[7]	0·664	—	—	0·664

Column 5 of Table I contains the values of μ/ρ for copper and aluminium calculated from the following formulæ arrived at by Hull and Rice* in their experiments on the absorption of the end radiations of a Coolidge tube:—

$$(\mu/\rho)\,\mathrm{Al} = 14{\cdot}9\,\lambda^3 + 0{\cdot}12.$$

$$(\mu/\rho)\,\mathrm{Cu} = 1{\cdot}50\,\lambda^3 + 0{\cdot}12.$$

where λ is the wave-length of the radiation ($0{\cdot}586 \times 10^{-8}$ cm. for the α-palladium line). These values of μ/ρ are also in agreement with those in the other columns.

The means of all the values are given in column 6 of the Table. The figures for the elements zinc to magnesium are more accurate than those for paper and water. The absorption in the case of these two substances is small, and in consequence the coefficient is not so easy to measure with accuracy.

In the diagram the logarithms of the mean value of μ/ρ are plotted as ordinates against the logarithms of the atomic numbers as abscissæ. A curve through the points is very nearly a straight line between the elements zinc and magnesium, but, beyond this point, as we proceed to the region of the lightest elements, the curve departs more and more from its straight-line course. If the absorption coefficients as determined by Auren be plotted in a similar manner, the curve obtained over the range of atomic numbers here employed shows exactly the same characteristics, but the divergence in the case of the light elements from the approximate linear relation existing between log μ/ρ and log N for elements between magnesium and zinc is rather more pronounced than in the present instance.

Before considering the effect which the scattering of the rays might have in determining the shape of the absorption curve as plotted here, it would be advisable to summarise briefly the laws of scattering as experimentally determined by Barkla.

The Scattering of X-rays.—When a beam of X-rays passes through matter it may lose its energy in two ways, namely, (1) by the production of corpuscular radiations and the characteristic radiations that accompany them, and (2) by the production of scattered radiation. In the former case, the quality of the radiation is changed, but in the latter case the quality remains unaltered. As a general rule these two processes take place simultaneously, but they are quite independent of each other.

Barkla has carried out extensive experiments on the scattering of X-rays, from which he has deduced many important laws governing the process of scattering. It is found that the scattering is dependent upon two main factors, (1) the atomic weight of the scatterer, and (2) the wave-length of the radiation.

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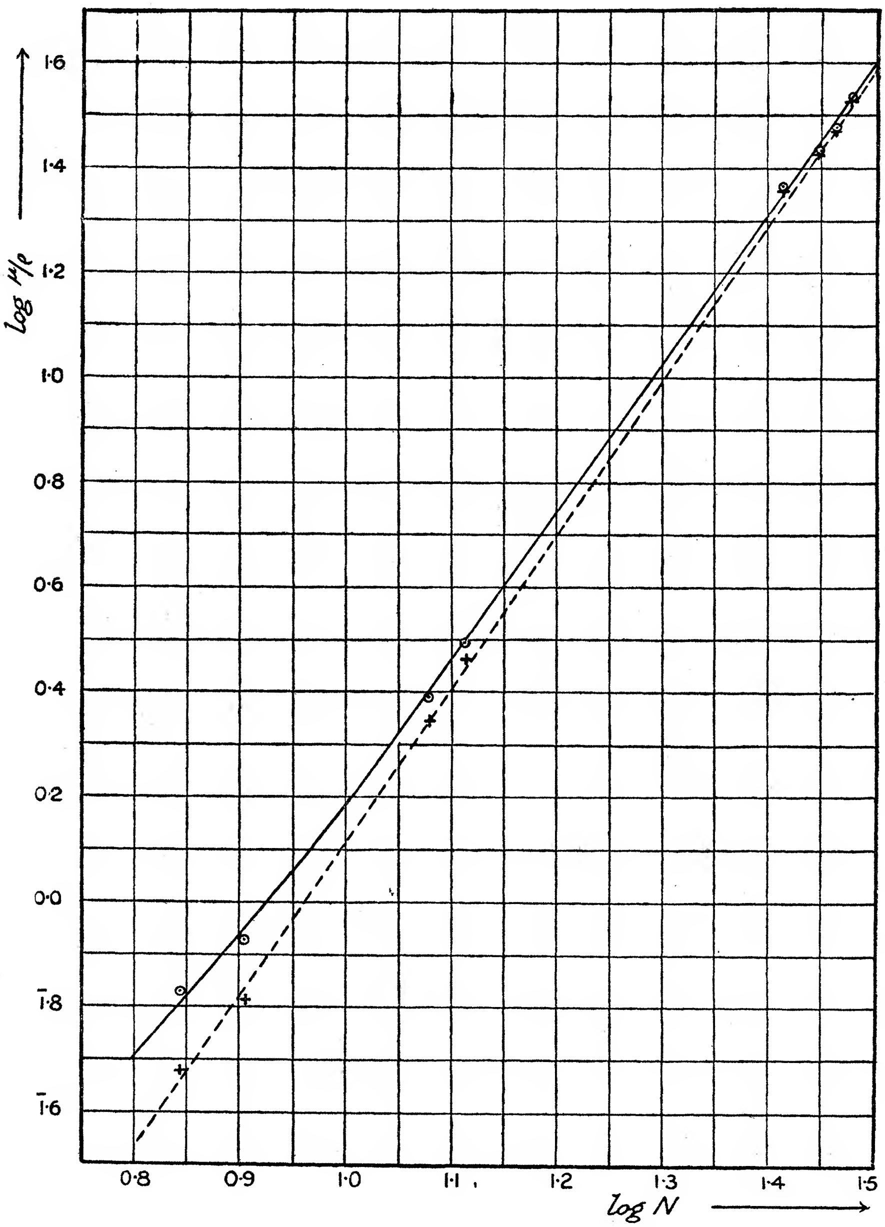
* Hull and Rice, 'Phys. Rev.,' vol. 8, p. 326 (1916).



Elements of low atomic weight scatter the same amount approximately mass for mass for radiations over wide limits of wave-length. There seems, however, to be a slight increase in the scattering with an increase in the wave-length of the radiation; this increase becomes more marked when the wave-length becomes so great as to be comparable with the size of the atom.

In the case of the heavier elements when the wave-length of the radiation is long, the scattering increases many-fold, but with short waves the mass scattering even in the heavier elements approaches equality with that in the light elements.

For the light elements when the wave-length of the radiation is short, the chief cause of loss of energy of the X-radiation may be put down to scattering; in general, it may be stated that the lower the atomic weight of the scatterer the greater is the proportion of loss of energy by scattering to the total loss of energy.

The scattering coefficient experimentally determined by Barkla in the case of light elements was found to have the value 0·2, and, as stated above, was found to be constant over wide limits of wave-length. This value 0·2 agrees almost perfectly with that obtained by calculation on the assumption that the number of electrons per atom is equal to the atomic number.

According to the simple electro-magnetic theory, the scattering coefficient should be a universal constant, independent entirely of the wave-length of the radiation scattered. Barkla's experiments show, however, that the coefficient is constant only for very short wave-lengths. Hull and Rice confirmed this result in their work on the absorption of X-radiations of very short wave-lengths in aluminium, copper, and lead, but the value of the scattering coefficient deduced by them from their experiments was somewhat lower than the above value found by Barkla. The wave-lengths employed ranged from $0{\cdot}147 \times 10^{-8}$ cm. to $0{\cdot}392 \times 10^{-8}$ cm. The greater of the two wave-lengths dealt with in the present work, namely, $0{\cdot}586 \times 10^{-8}$ cm., is a little outside this range, but it will be assumed that the scattering coefficient for this wave also is constant for all the elements used, and that its value is 0·2, the value found by Barkla for the light elements.

Let us now find what effect the correction for scattering produces on the shape of the absorption curve. The absorption coefficients plotted in the diagram are the total absorption coefficients, which include both the scattering and the fluorescent coefficients. If τ/ρ is the fluorescent absorption coefficient and σ/ρ the scattering absorption coefficient, then the total absorption coefficient is given by the relation $\mu/\rho = \tau/\rho + \sigma/\rho$. In the present case, σ/ρ is assumed to be constant and equal to 0·2. Plotting the logarithms of the values of τ/ρ obtained from this relation on this assumption, against the logarithms of the atomic numbers of the absorbing atoms, we find that the points all lie very approximately along a straight line. The line is dotted in the diagram above. This line gives the index 3 approximately, so that the relation between τ/ρ and N may be approximately expressed by the equation $\tau/\rho = C'N^3$, where C' is a constant. If, however, the atomic fluorescent absorption coefficient is calculated in each case, it is found that the results are more accurately expressed by the equation

$$\text{Atomic fluorescent absorption coefficient} = CN^4.$$

This result is slightly different from that of Bragg and Pierce; the difference between the two relations is not so marked in the case of the heavier atoms, because the scattering coefficient is small compared with the fluorescent coefficient, but it becomes very appreciable for elements of low atomic weight, in which case the absorption by scattering becomes the prominent part of the total absorption.

To test the validity of this law, it will be used to calculate the molecular absorption coefficients which have been experimentally determined by Auren. To do this, we have to consider in detail the transformation of absorption coefficients obtained with one wave-length to those which should be obtained with a radiation of another wave-length. This transformation can be carried out without much difficulty by the use of the relation connecting absorption coefficient with wave-length.

The Relation between Absorption Coefficient and Wave-length of the Radiation Absorbed.—It was pointed out by the writer* a few years ago that the connection between the absorption coefficient and the atomic weight of the radiator whose characteristic radiation was employed, could be approximately expressed by a very simple relation; the absorption coefficient was found to be approximately inversely proportional to the fifth power of the atomic weight of the radiator. This relation was arrived at before definite wave-lengths were assigned to X-rays. Since the wave-length of the radiation characteristic of a certain element has been found to be approximately inversely proportional to the square of the atomic weight of that element, the above relation expressed in terms of wave-length takes the form $\mu/\rho \propto \lambda^{5/2}$, which accounts for the factor $\lambda^{5/2}$ appearing in the general law written down by Bragg and Pierce. Further experiment† has shown that the relation $\tau/\rho = a\lambda^3$ is a more accurate representation of the observed results (where τ/ρ is the fluorescent absorption coefficient). This law is found to hold for all wave-lengths except those in the immediate vicinity of an absorption band, when the value of the constant a changes suddenly. If the fluorescent absorption coefficient of a certain substance is known for one wave-length, by means of this relation it can be calculated for any other wave-length so long as that substance does not selectively absorb any radiation in the region between the two wave-lengths considered. Also, since it is assumed here that the scattering coefficient is constant for all substances in the case of the two wave-lengths with which we are concerned, the total absorption coefficient is also determined.

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* Owen, 'Roy. Soc. Proc.,' A, vol. 86, p. 426 (1912).

† Hull and Rice, *loc. cit.*; Barkla and White, 'Phil. Mag.,' vol. 34, p. 270 (1917); Owen, 'Roy. Soc. Proc.,' A, vol. 94, p. 339 (1918).

Calculation of Results.—Table II contains the values of τ/ρ for the most common elements from hydrogen to bromine for the α-line of palladium ($\lambda = 0{\cdot}586 \times 10^{-8}$ cm.). The values have been taken direct from a straight line corresponding to the dotted line in fig. 1, which had been drawn on a large scale. The mass of the atoms and the calculated values of the atomic total absorption coefficients are also included in the Table.

Table II.

$\lambda = 0{\cdot}586 \times 10^{-8}$.

Element.	Atomic number.	Fluorescent absorption coefficient (τ/ρ).	Total absorption coefficient (μ/ρ).	Mass of absorbing atom (w).	Atomic total absorption coefficient ($\mu/\rho \, . \, w$).
H	1	0·0015	0·2015	$1{\cdot}64 \times 10^{-24}$	$0{\cdot}331 \times 10^{-24}$
C	6	0·301	0·501	19·67	9·85
N	7	0·468	0·668	23·00	15·34
O	8	0·687	0·887	26·25	23·28
F	9	0·966	1·166	31·15	36·28
Na	11	1·726	1·926	37·74	72·6
Mg	12	2·239	2·439	39·84	96·9
Al	13	2·805	3·005	44·45	133·7
Si	14	3·516	3·716	46·4	172·1
P	15	4·295	4·495	50·9	228·6
S	16	5·212	5·412	52·6	284·5
Cl	17	6·194	6·394	58·1	371·6
K	19	8·551	8·751	64·1	561·0
Ca	20	9·977	10·18	65·8	669·0
Cr	24	16·98	17·18	85·3	1463
Mn	25	19·05	19·25	90·0	1732
Fe	26	21·58	21·78	91·6	1992
Co	27	24·10	24·30	96·7	2346
Ni	28	26·79	26·99	96·3	2600
Cu	29	29·72	29·92	104·1	3112
Zn	30	32·81	33·01	107·1	3538
As	33	43·05	43·25	122·9	5315
Se	34	46·88	47·08	129·9	6115
Br	35	51·40	51·60	131·0	6755

In order to calculate the molecular absorption coefficient of a complex molecule from the atomic absorption coefficients of the atoms composing that molecule, we shall assume, as Auren did, that the total absorption coefficient of the molecule may be obtained by adding together the total absorption coefficients of its atoms.

Let $(\mu/\rho)_1$, $(\tau/\rho)_1$, and $(\sigma/\rho)_1$ be the total absorption coefficient, the fluorescent absorption coefficient, and the scattering coefficient respectively for the wave-length $0{\cdot}586\times10^{-8}$ cm., for any element, and let the same notation with the suffix 2 denote the same quantities for the wave-length $0{\cdot}35\times10^{-8}$ cm., which is the mean wave-length of the radiation used by Auren in his investigation.

Since $$(\tau/\rho)_1\lambda_2^3=(\tau/\rho)_2\lambda_1^3,$$

then $$(\tau/\rho)_2=0{\cdot}213\,(\tau/\rho)_1,$$

and since $$(\sigma/\rho)_1=(\sigma/\rho)_2=0{\cdot}2,$$

then $$(\mu/\rho)_2=0{\cdot}213\,(\mu/\rho)_1+0{\cdot}1574,$$

which is the relation connecting the total absorption coefficients of any element for the wave-lengths $0{\cdot}586\times10^{-8}$ cm. and $0{\cdot}35\times10^{-8}$ cm. Let t_a' and t_a'' denote the atomic total absorption coefficients for these two wave-lengths respectively.

Then $$t_a''=0{\cdot}213\,t_a'+0{\cdot}1574\,w,$$

where w is the mass of the atom.

If t_m' and t_m'' denote the molecular total absorption coefficients, then, by the additive law that we are assuming, it follows that

$$t_m''=0{\cdot}213\,t_m'+0{\cdot}1574\,m \qquad (1)$$

where m is the mass of the molecule.

Knowing the molecular total absorption coefficient (t_m') of any substance for the wave-length $0{\cdot}586\times10^{-8}$ cm., we can calculate by the aid of equation (1) the molecular total absorption coefficient for the wave-length $0{\cdot}35\times10^{-8}$ cm.

Consider, for example, the molecule NaCl.

From Table II we find that the atomic total absorption coefficients of the atoms Na and Cl for the wave-length $0{\cdot}586\times10^{-8}$ cm. are $72{\cdot}6\times10^{-24}$ and $371{\cdot}6\times10^{-24}$ respectively.

The molecular total absorption coefficient (t_m') is, therefore, $444{\cdot}2\times10^{-24}$.

The mass of the molecule $(m)=58{\cdot}46\times1{\cdot}64\times10^{-24}$.

Substituting these values in (1) we get

$$t_m''=109{\cdot}59\times10^{-24},$$

which is the figure that appears in Table III.

The molecular total absorption coefficients of all the substances investigated by Auren (except those containing atoms heavier than bromine, which were omitted because of their proximity to a critical region of the α-palladium line) were calculated in this manner. A list of the calculated values is contained in Table III. Column 5 of this Table contains the ratio of the calculated values of the molecular total absorption coefficient of any substance to that of water. These figures are directly comparable with the experimental values obtained by Auren, which are included for comparison in Column 6 of the Table.

Table III.

Absorbing substance.	Formula weight.	Molecular total absorption co-efficient. $\lambda = 0{\cdot}586 \times 10^{-8}$ cm.	Calculated molecular total absorption co-efficient. $\lambda = 0{\cdot}35 \times 10^{-8}$ cm.	Molecular total absorption co-efficient relative to that of water.	
		$t_m' \times 10^{24}$.	$t_m'' \times 10^{24}$.	Calculated.	Observed (Auren).
H_2O	18·01	23·94	9·749	1·0	1·0
$NaClO_3$	106·46	514·2	136·9	14·02	14·2
NaCl	58·46	444·2	109·6	11·24	11·5
NaOH	40·01	96·21	30·82	3·09	2·77
C_6H_6	78·05	61·09	33·16	3·40	2·97
CH_4O	32·03	34·45	15·60	1·60	1·56
$C_4H_{10}O$	74·08	65·99	33·18	3·40	3·32
C_3H_6O	58·05	54·82	26·65	2·73	2·58
C_3H_8O	60·06	55·48	27·32	2·80	2·69
$(C_2H_5)_4Si$	144·46	257·52	92·13	9·44	8·56
$(C_6H_5)Si(CH_3)_3$	150·43	265·38	95·39	9·78	9·06
HNO_3	63·02	85·51	34·49	3·54	3·36
NH_4NO_3	80·05	101·84	42·36	4·34	4·17
$C_6H_5NO_2$	123·05	122·66	57·89	5·94	5·40
C_5H_5N	79·05	66·24	34·52	3·54	3·14
$C_6H_5NH_2$	93·09	76·76	40·37	4·14	3·63
$MgCl_2$	95·24	840·1	203·54	20·87	22·5
$Al_2(SO_4)_3$	342·41	1400·3	386·64	39·65	41·0
H_3PO_4	98·06	322·71	94·05	9·65	9·43
H_2SO_4	98·09	378·29	105·90	10·86	11·48
HCl	36·47	371·93	88·61	9·09	9·55
KCl	74·56	932·6	217·89	22·34	20·7
$CaCl_2$	111·01	1412·2	329·45	33·8	33·4
$CrCl_3$	158·38	2577·8	589·95	60·5	52·6
$MnCl_2$	125·85	2475·2	559·70	57·4	60·4
$KFe(SO_4)_2$	287·09	3308·2	778·76	79·9	79·4
$NiCl_2$	129·60	3343·2	745·56	76·4	78·4
$CoCl_2$	129·89	3089·2	691·53	70·9	72·9
$CuCl_2$	134·49	3855·2	855·87	87·8	84·1
$ZnCl_2$	136·29	4281·2	947·20	97·1	96·3
$ZnSO_4$	161·44	3915·6	875·40	89·8	84·8
Na_2HAsO_4	185·97	5553·7	1230·0	126·1	136·0
KBr	119·02	7316·0	1587·7	162·8	165·0
$FeSO_4$	151·92	2369·6	544·20	55·8	—

It will be noticed that for all the substances investigated the agreement between the experimental values and the values of the molecular absorption coefficients calculated along the lines indicated here is remarkably good, in view of the possible error in the determination of the mean value of the wave-length of the direct radiation used by Auren, and also the uncertainty attaching to the value of the scattering coefficient, which has been assumed to have the value 0·2 over the whole range of elements from hydrogen to bromine for the wave-lengths concerned.

From the examples cited by Auren in his paper, it would appear that the difference between calculated and observed values is well within the range of variation of the experimental values of the molecular absorption coefficient of a given molecule as determined from solutions of different concentrations. For instance, the observed values of the relative molecular absorption coefficient for the molecule KCl range from 18·2 to 23·6; the calculated value is 22·3.

The salt $FeSO_4$ is not included in the list of substances contained in Auren's Table; it is excluded because a general rise was found in the values of the relative molecular absorption coefficient for this salt as the concentration of the solution was decreased. This variation is accounted for by the fact that the salt, being oxidised by contact with air and hydrolysed by dilution, passes into a colloidal state. The values of the relative molecular absorption coefficient for this molecule, given by Auren in a separate Table, vary from 53·0 for a solution of the concentration 1·08 gramme-molecules per litre to 58·4 for that of concentration 0·133 gramme-molecule per litre. The value obtained for this molecule from the present results by calculation is 55·8, and is almost exactly the mean of all the observed values given.

The validity of the relation that has been arrived at may be further tested in the case of paraffin wax, which is a substance containing a comparatively high percentage of hydrogen by weight. The chemical formula of this substance may be written as $C_{22}H_{46}$ or $C_{32}H_{66}$. Either formula gives by calculation the value 0·456 for the total absorption coefficient of this substance for the wave-length $0·586 \times 10^{-8}$ cm. The value obtained by experiment is 0·425. The agreement between these two figures is good in view of the fact that it is difficult to measure the absorption coefficient of this substance with great accuracy.

Table IV gives the observed and calculated results for the three substances water, filter paper, and paraffin wax, for the wave-length $0·586 \times 10^{-8}$ cm.

Table IV.

Substance.	Formula weight.	μ/ρ for $\lambda = 0·586 \times 10^{-8}$ cm.	
		Observed.	Calculated.
Water	H_2O	0·84	0·81
Paper	$n\,(C_6H_{10}O_5)$	0·66	0·67
Paraffin wax	$C_{22}H_{46}$ or $C_{32}H_{66}$	0·43	0·46

Conclusions.—The experimental values of the mass absorption coefficients of elements ranging from aluminium to zinc for the wave-length

$0 \cdot 586 \times 10^{-8}$ cm. observed by Bragg and Pierce have been confirmed, and it is shown that the values of the relative molecular total absorption coefficients of different substances experimentally determined by Auren for a radiation of wave-length $0 \cdot 35 \times 10^{-8}$ cm., may be calculated from these values by making a suitable allowance for the scattering of the radiation.

The results indicate that the atomic fluorescent absorption coefficient is directly proportional to the fourth power of the atomic number of the absorbing atom, which may be represented by the following equation:—

$$f_a = C_1 N^4, \tag{2}$$

where f_a is the atomic fluorescent absorption coefficient, N the atomic number, and C_1 a constant over ranges outside critical regions.

It is known also that the fluorescent absorption coefficient varies as the cube of the wave-length of the radiation absorbed, so that

$$\tau/\rho = C_2 \lambda^3. \tag{3}$$

Combining these two relations we get the following general relation connecting atomic fluorescent absorption coefficient, atomic number of the absorber, and wave-length of absorbed radiation:—

$$f_a = C N^4 \lambda^3, \tag{4}$$

where C is a constant over certain ranges but changes abruptly at critical points. This relation is independent of the scattering coefficient and refers only to the loss of energy of X-radiation by the production of corpuscular radiations and the fluorescent X-radiations that accompany them.

The calculations carried out in this paper are based on equation (4). To arrive at the molecular total absorption coefficient of any molecule, it has been necessary to make the two following assumptions:—

(1) The molecular total absorption coefficient of a complex molecule is additively determined from the atomic total absorption coefficients of its constituent atoms.

(2) The mass scattering coefficient of all the elements from hydrogen to bromine has a constant value of 0·2.

The first assumption implies that the absorption of radiation by an atom is the same whether or not that atom is in combination with other atoms. This assumption is fully justified by the results of different investigators.

There seems to be some uncertainty in regard to the second assumption. For instance, Barkla and Dunlop* find for the wave-length $0 \cdot 316 \times 10^{-8}$ cm. the following values:—

$$\left(\frac{\sigma}{\rho}\right)_{\mathrm{Cu}} \Big/ \left(\frac{\sigma}{\rho}\right)_{\mathrm{Al}} = 1 \cdot 12; \quad \left(\frac{\sigma}{\rho}\right)_{\mathrm{Pb}} \Big/ \left(\frac{\sigma}{\rho}\right)_{\mathrm{Al}} = 2 \cdot 65,$$

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* Barkla and Dunlop, 'Phil. Mag.,' vol. 31, p. 229 (1916).

the relative scattering for lead being more than twice that for copper. (For longer waves these relative values show marked increases.) Hull and Rice,[*] on the other hand, find that the relative scattering with this radiation has the same value in each case, and is equal to unity. In view of this irregularity it was deemed advisable to assume the scattering coefficient to be constant for all the elements employed for the two wave-lengths dealt with, namely $0{\cdot}35 \times 10^{-8}$ cm. and $0{\cdot}586 \times 10^{-8}$ cm. There is some ground for making this assumption in the fact that on the electro-magnetic theory this quantity should be an universal constant. The absolute value 0·2 was taken because Barkla has made many determinations of this quantity for light elements and has invariably found this value for it. Furthermore it is the value that, when substituted in Sir J. J. Thomson's expression for the loss of energy by scattering, gives the value at present accepted for the number of electrons in the atom. The agreement found here between calculated and observed values lends some support to the validity of the assumption. It is possible, however, that the agreement between calculated and observed values might be even better than in the present instance if it were known exactly how the scattering coefficient varies with the wave-length of the radiation scattered, and also the mass of the atom, and an accurate allowance be made for this in the calculations.[†]

A method of measuring coefficients of scattering is suggested by the results of this investigation. We have found that the atomic fluorescent absorption coefficient is proportional to the fourth power of the atomic number of the absorber; we know also the value of the scattering coefficient for light elements. If then an accurate method of measuring total absorption coefficients be employed, by the aid of these two facts, the variation of the scattering coefficient can be investigated for any wave-length over any range of atomic numbers.

Summary.

(1) The absorption coefficients of a number of substances for a radiation of wave-length $0{\cdot}586 \times 10^{-8}$ cm. (the α-line of palladium) have been determined, and the values obtained confirm those of Bragg and Pierce in the case of elements used in common.

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[*] Hull and Rice, *loc. cit.*

[†] It might be mentioned that when the value of the scattering coefficient for hydrogen was taken to be twice that of other light elements, and the calculations proceeded with in a manner similar to that described here, the agreement between the observed and calculated values of the molecular total absorption coefficient was not so good as in the case investigated when the value of the scattering coefficient of hydrogen was taken to be the same as that of other light elements.

(2) The atomic fluorescent absorption coefficient is proportional approximately to the fourth power of the atomic number of the absorber.

(3) The following relation exists between the atomic fluorescent absorption coefficient, atomic number of the absorber, and the wave-length of the radiation absorbed:

$$f_a = \mathrm{C}\mathrm{N}^4\lambda^3,$$

where C is a constant over certain ranges, but changes abruptly at critical points.

This relation is independent of the scattering coefficient; it deals only with the loss of energy of X-radiation by the production of corpuscular radiations and the fluorescent X-radiations that accompany them.

(4) Calculations based on the above general relation show that the molecular total absorption coefficients of different substances observed by Auren with radiation of wave-length $0{\cdot}35 \times 10^{-8}$ cm. may be deduced very approximately from the atomic total absorption coefficients obtained for different elements with radiation of wave-length $0{\cdot}586 \times 10^{-8}$ cm., if the coefficient of scattering be assumed to have a constant value of 0·2 for all elements from hydrogen to bromine for both these radiations.

I desire to express my indebtedness to Prof. A. W. Porter, F.R.S., for the help he has given me throughout the course of the investigation.